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Density functional theory of adsorption in pillared slit-like pores

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Abstract

We propose a density functional theory to describe adsorption of Lennard–Jones fluid in pillared slit like pores. Specifically, the pillars are built of chains that are bonded by their ends to the opposite pore walls. The approach we propose combines theory of quenched–annealed systems and theory of nonuniform fluids involving chain molecules. We compare the results of theoretical predictions with grand canonical ensemble Monte Carlo simulations and compute theoretical capillary condensation phase diagrams for several model systems.

Keywords: Adsorption; Pillared pore; Density functional theory; Monte Carlo simulation

1. Introduction

In recent years a number of researchers have investigated adsorption in synthetic pillared clays [1–6]. The synthesis of pillared clays was originally suggested by Barrer and McLeod [7], who inserted specific molecules into clay minerals to prop apart the aluminosilicate sheets, thereby producing larger pores than those found in natural clays. In general, pillared clays are obtained by exchanging the charge-compensating cations present in the interlamellar space of the clays with hydroxy-metal polycations. On calcining, the inserted polycations yield rigid, thermally stable oxide species, named pillars. The porous structure of pillared adsorbents is characterized by the so-called interlayer and interpillar spacings. These spacings can be controlled to a large extent by adjusting different parameters involved in the synthesis process [8,9].

Commonly used approaches for the description of gas adsorption by pillared adsorbents have been based on the application of standard methods to study adsorption in nonuniform pores [9–14]. On the other hand, molecular simulations of adsorption and diffusion in model pillared clays were initiated by Sahimi and co-workers [15–17], who used grand canonical ensemble Monte Carlo and molecular dynamics simulations to study adsorption and diffusion of gas molecules. Later, the results of computer simulations of adsorption by pillared adsorbents were reported in several works [18–26].

In simulation studies of adsorption, a model of Yi et al. [15–17] with uniform distribution of pillars between two walls has usually been used. According to this model the pore walls are "connected" by chains consisting of M tangentially jointed Lennard–Jones spheres of identical diameter, $\sigma^{(CC)}$. Both ends of the pillars are "pinned" at two opposite surfaces. In the original model the chains are considered as rigid and the distance between two pore walls is determined by the chain length, $H = M\sigma^{(CC)}$. Moreover, the pillars occupy the position on a lattice and form a periodic structure. Thus, the density distribution of an adsorbate is a periodic function that vary in three-dimensions. Unfortunately, a theory for such a model is difficult to be implemented numerically. Therefore, an alternative treatment that relies on the introduction of a one-dimensional "effective" local density of an adsorbate has serious advantages; in particular all the integrals involved in the procedure would be one-fold only.

Quite recently Borówko et al. [27] proposed the application of a version of density functional approach of adsorption of chain particles that was developed by Wu an co-workers [28–30] to describe adsorption of hard-sphere mixtures on a surface covered with a brush formed of chain molecules. A comparison with Monte Carlo simulation indicated that the

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theory reproduced precisely simulation data. A similar theory has been next employed to study adsorption and phase transitions in slit like pores whose walls were modified by attached (pre-adsorbed) chain particles [31]. The success of the above mentioned approaches has stimulated us to propose a density functional theory of adsorption of spherical particles in pillared-like pores. Similarly as in previous works [27,31], the proposed method is based on the developments of Wu and co-workers [28–30]. Moreover, a rigid structure of pillars is described in terms of a generalized density-functional approach of quenched–annealed mixtures of Schmidt [32–34]. To test the theory, we compare the results of theoretical predictions with Grand Canonical ensemble Monte Carlo simulation data.

2. Theory

The pillared adsorbent is prepared by binding of a selected number of chain molecules to the pore walls. Following the model of Yi et al. [15–17] each pillar consists of M tangentially jointed spherical segments of the diameter $\sigma^{(CC)}$ each. Two terminating segments (i.e., the segments $j = 1$ and $j = M$) are pinned at the opposite pore walls. The pore walls are at a distance H apart. The most often studied model assumes that the pillars are completely rigid and that the pore width is related to the length of pillars via $H = M\sigma^{(CC)}$. However, one can also consider a more general situation in which $H \leqslant M\sigma^{(CC)}$.

The terminating segment interact with its "host" surface via a short-range, strongly attractive potential

$$v_1^{(C)}(z) = \begin{cases} \infty, & \text{for } z < \sigma^{(CC)}/2, \\ \mathcal{E}\delta(z - \sigma^{(CC)}/2), & \text{otherwise} \end{cases} \tag{1}$$

and

$$v_M^{(C)}(z) = \begin{cases} \infty, & \text{for } z > H - \sigma^{(CC)}/2, \\ \mathcal{E}\delta(z - H + \sigma^{(CC)}/2), & \text{otherwise,} \end{cases} \tag{2}$$

where the energy of the interaction $\mathcal{E}$ is very high. All the remaining segments interact with the pore wall via hard-wall potentials

$$v_i^{(C)}(z) = \begin{cases} \infty, & z \leqslant \sigma^{(CC)}/2,\ z \geqslant H - \sigma^{(CC)}/2, \\ 0, & \text{otherwise} \end{cases} \tag{3}$$

for $i = 2, 3, \ldots, M - 1$.

The connectivity of a chain is ensured by imposing the bonding potential between two adjacent segments, v_b. The total bonding potential satisfies the relation [28]

$$\exp\bigl[-\beta V_b(\mathbf{R})\bigr] = \prod_{i=1}^{M-1} \delta\bigl(|\mathbf{r}_{i+1} - \mathbf{r}_i| - \sigma^{(CC)}\bigr)/4\pi\bigl(\sigma^{(CC)}\bigr)^2, \tag{4}$$

where $\mathbf{R} \equiv (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_M)$ denotes a set of coordinates describing the segment positions. Therefore for $H \leqslant M\sigma^{(CC)}$ the positions of all inner segments are restricted by the positions of the terminating segments and by the binding potential. Obviously, for $H = M\sigma^{(CC)}$ none of the segments can change the position with respect to its neighbors.

The process of the modification of pores is completely separated from the second step that relies on the adsorption of other molecules. The equilibrium structure of the chains inside the pore is characterized by the density distribution $\rho^{(C)}(\mathbf{R})$. In general, the function $\rho^{(C)}(\mathbf{R})$ can be evaluated within the framework of the Yu and Wu theory [27–31]. This theory introduces the segment densities, $\rho_{s,j}^{(C)}$, and the total segment density of chains, $\rho_s^{(C)}$, via

$$\rho_s^{(C)}(\mathbf{r}) = \sum_{j=1}^{M} \rho_{s,j}^{(C)}(\mathbf{r}) = \sum_{j=1}^{M} \int \mathrm{d}\mathbf{R}\,\delta(\mathbf{r} - \mathbf{r}_j)\rho^{(C)}(\mathbf{R}). \tag{5}$$

Because the evaluation of the profiles $\rho_{s,j}^{(C)}$ has been discussed in numerous works we refer the reader to the original publications [28–30].

The calculations outlined in the papers cited above must be carried out assuming a constant number of the confined chains, i.e., imposing the condition [27]

$$\int_{V_p} \mathrm{d}\mathbf{r}\rho_{s,j}^{(C)}(r) = \rho_M, \tag{6}$$

where the integration is over the entire pore volume V_p and ρ_M is the average number of chains (pillars) in the pore. Obviously, in the limiting case of $H = M\sigma^{(CC)}$ the segment density profiles are given by

$$\rho_{s,i}^{(C)}(z) = \rho_M\delta\biggl(z + \biggl[\biggl(i - \frac{1}{2}\biggr)\sigma^{(CC)}\biggr]\biggr). \tag{7}$$

The imposed condition (6) causes that the exact value of the energy $\mathcal{E}$ is irrelevant.

After preparing the pore, the configuration of the chain particles is quenched. Therefore, the adsorption of spherical molecules can be described by employing a generalized version of the theory of quenched–annealed systems that was developed by Schmidt [32–34]. To write down the relevant equation we define the model of adsorption of spherical molecules first.

The spherical species S are Lennard–Jones molecules of diameter $\sigma^{(SS)}$. The process of adsorption takes place from a reservoir containing one-component bulk fluid phase at a fixed chemical potential μ. The spherical molecules of a fluid interact with each wall via the potential

$$v^{(S)}(z) = 2\pi\rho_w\varepsilon_{Sw}\bigl[\sigma^{(Sw)}\bigr]^2\Delta\biggl[0.4\bigl(\sigma^{(Sw)}/z\bigr)^{10} + \bigl(\sigma^{(Sw)}/z\bigr)^4 - \frac{(\sigma^{(Sw)})^4}{3\Delta(0.61\Delta + z)^3}\biggr], \tag{8}$$

where z is the distance from the wall, ρ_w is the number density of the solid wall, Δ is the distance between the lattice planes of the wall and ε_{Sw} and $\sigma^{(Sw)}$ are the energy and size parameters. Obviously, the molecule–pore potential is $v_1^{(S)}(z) = v^{(S)}(z) + v^{(S)}(H - z)$. The potential (8) was developed by Steele [35] by assuming the solid to be built of layers of atoms of diameters $\sigma^{(ww)}$ and by replacing the summation of the interactions between an adsorbate molecule and surface atoms located within a given plane by the integration. Following Cao and Wang [20,22,23] we assume that $\rho_w = 114\ \text{nm}^{-3}$ and $\Delta = 0.335$ nm. Although the above parameters are appropriate for the graphite